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(54) Title: PERMANENT MAGNETIC MATERIALS OF THE R-FE-B TYPE AND PROCESS OF MANUFACTURE

(57) Abstract: An Fe-B-R type permanent magnetic, consisting of: 13-19 atomic % R, where R essentially consists of a mixture of rare earth elements Nd and/or Pr, and Ce, where Ce is between 0.2 and 5.0 wt. % of R; 4-20 atomic % B, and the balance comprising Fe. In a preferred aspect, R comprises 15-16 atomic % B; of which Ce is approximately 0.5 % and the remaining rare earths Pr and Nd are in a ratio of 3:1. A process of producing an Fe-B-R permanent magnet as described above, and an Fe-B-R magnetic material made by such process, are also disclosed.

PERMANENT MAGNETIC MATERIALS OF THE Fe-B-R TYPE,  
CONTAINING Ce and Nd AND/OR Pr, AND PROCESS OF  
MANUFACTURE

BACKGROUND OF THE INVENTION

5           The present invention relates to magnetic material compositions and a process for their manufacture, and more particularly performance magnetic material of the iron-boron-rare earth type (Fe-B-R).

          Use of high performance permanent magnets of Fe-B-R type, where R is a rare earth element containing high concentrations of the element  
10   Neodymium (Nd) has become common in industry since the early 1980's. For example, computer hardware manufacturers who manufacture small footprint, large capacity computer data storage and retrieval hardware need permanent magnets in such devices. Due to severe size and weight restrictions inherent in such data storage devices, the permanent magnets  
15   contained therein must be relatively small yet have very strong magnetic properties to generate the required magnetic field. This has necessitated the use of very high performance Fe-B-R rare-earth permanent magnets within such devices.

          In addition, medical diagnostic devices in the medical field,  
20   namely, magnetic resonance imaging (MRI) devices employ vast quantities (up to 1.5 tons) of permanent magnetic material, typically Fe-B-R magnets which contain high percentages of the rare earth Nd as the rare earth component.

          Accordingly, due to the sale of these devices since the early  
25   1980's employing Fe-B-R permanent magnets wherein the rare earth

component is principally comprised of Nd, the worldwide demand for Nd has increased. As a result, the cost of the raw material Nd used in manufacture of such permanent magnets has greatly increased.

5 A real need has arisen to develop Fe-B-R magnets of substantially equal performance, which utilize less Nd to thereby reduce the cost of the manufacture of such magnets and the devices which contain such magnets.

Permanent magnets of the Fe-B-R type, where R is one or more rare earth elements of which at least 50% of R is Nd and/or Praseodymium (Pr), are known. For example, U.S. Patents 4,684,406 and 4,597,938 both teach 10 a high performance sintered permanent magnetic material of the Fe-B-R type. Such patents teach a high performance magnet consisting of, by atomic percent, (i) 12.5%-20% R wherein R is at least one rare earth element (selected from the group consisting of Nd, Pr, La, Ce, Tb, Dy, Ho, Er, Eu, Sm, Gd, Pm, 15 Tm, Yb, Lu and Y) and at least 50% of R consists of Nd and/or Pr; (ii) 4-20%B; and (iii) the balance Fe with impurities. Likewise, as may be seen from U.S. 4,597,938, U.S. 4,975,130 and U.S. 4,684,606, such patents teach a process of preparing such a permanent magnet comprising forming powders of alloys of the above composition; melting same to form an ingot; pulverizing the ingot 20 to form an alloy powder having a mean particle size from 0.3 to 80 microns; compacting such powder at a pressure of 0.5 to 8 Ton/cm<sup>2</sup>; subjecting the compacted body to a magnetic field of about 7 to 13 kOe; and lastly sintering at a temperature between 900 to 1,200 C (preferably 1,000 to 1,180 C). A permanent magnet prepared in the above fashion specifically comprised of 77 Fe-9 B-9 Nd-5 Pr (wherein Nd and Pr together comprise the rare earth 25 component), sintered at 1,120 C for four hours in an inert atmosphere can

acquire a high maximum energy product  $(BH)_{\max}$  of approximately 31.0 MGOe. Likewise, a permanent magnet comprised of 79 Fe-7 B-14 Nd, sintered at 1,120 °C for one hour at (atmosphere), can acquire a maximum energy product  $(BH)_{\max}$  of approximately 33.8 MGOe (ref. Table 1, U.S. 4,975,130). A sintered permanent magnet comprising 77Fe-7B-16Pr, sintered at 1,040 °C in a vacuum at  $1 \times 10^{-4}$  torr for two hours can be produced having a maximum energy product somewhat less, namely, 24.5 MGOe.

None of these prior art patents disclose or suggest what significance, if any, the amount of Ce present or the concentration of Ce as part of R may have on Fe-B-R magnet performance. Nor does the prior art teach or suggest ranges of concentrations of Ce which may form part of the rare earth component of an Fe-B-R magnet in substitution for Nd which will give equal or better magnetic performance of an Fe-B-(Nd and/or Pr) permanent magnet.

## SUMMARY OF THE INVENTION

Applicants have discovered that relatively small percentages of Cerium, which in any event usually naturally occur in rare earth deposits containing Nd, may be included in certain defined percentages as part of the rare earth component "R" of an Fe-B-R magnet. R additionally comprises 70-76% Pr, 29.8-23.8% Nd and up to and including 5% Ce with no significant or only slight decrease in the magnetic performance of the resultant permanent magnet.

The applicants have further discovered that when certain low percentages of Cerium-(0.5% wt. of-R)-are used in manufacture of an Fe-B-R permanent magnet in substitution of Nd, further substitution of Nd may

further be made with Pr up to 76% which further substitution, particularly at Pr = 75%, will not reduce, and indeed appears to substantially equal or even enhance, the magnetic performance characteristics over a magnetic material made up of the same total percentage of rare earth elements but lacking Ce, or having Ce but having higher concentrations of Nd.

By substitution of portions of Nd with specific small percentages of Ce and greater amounts of Ce in accordance with the invention herein disclosed, significant cost savings can be achieved in the manufacture of high performance permanent magnets of the Fe-B-R type, while substantially maintaining the magnetic performance of the magnet. Even in respect of certain concentrations of added or entrained Ce which may cause a reduction in the magnetic performance of the Fe-B-R magnetic material as compared with Fe-B-R magnetic material which employs substantially pure Nd, additional magnetic material having Ce and Pr as described herein can be used so as to make up the deficit in strength of magnetic field required in an MRI device.

Accordingly, in one broad aspect the applicants' invention comprises a high performance permanent magnetic material of the Fe-B-R type, said material essentially consisting of:

(i) 13-19 atomic % R, where R comprises a mixture of rare earth elements Nd, Pr, and Ce wherein Ce is between approximately 0.2% and no more than 5.0 wt. % of R and Pr is between 70-76% and 29.8-23.8% Nd;

(ii) 4-20 atomic % B;

25(iii)

the balance comprising Fe with impurities.

In preferred embodiments, the Fe-B-R magnet of the present invention essentially consisted of, by atomic %, 15-16% R, with Ce comprising 0.5-3 wt. %, and preferably 0.5%, with the remainder of R essentially consisting of Pr and/or Nd, preferably in the order of about 71.6% Pr and 24.9 % Nd, i.e. a 3:1 ratio.

The present invention further comprises a sintered permanent magnetic material of the Fe-B-R type when made in accordance with the following process, namely:

- (a) preparing a metallic powder having a mean particle size of 0.3-80 microns, said metallic powder formed from a composition essentially consisting of 15-16 atomic % R, wherein R essentially consists of the light rare earths Nd, Pr, and Ce, wherein Ce is between 0.2-5.0 wt. % of said R, the balance of R essentially consisting of 29.8-23.8% Nd and 70-76% Pr; 4-8 atomic % B, and at least 52 atomic % Fe;
- (b) compacting said powder at a pressure of at least 1.5 ton/cm<sup>2</sup>;
- (c) sintering the resulted body at a temperature of 900-1200 °C in a non-oxidizing or reducing atmosphere.

In addition, the applicants have found that while adding Cerium generally tends to decrease magnetic performance of Fe-B-R magnets having only Nd, by substituting Pr for Nd where Ce concentration is low will cause a substantial restoration of lost magnetic performance. Accordingly, the applicant has found that using low concentrations of Ce (0.5% wt.) of R with the balance of R essentially consisting of approximately 74.6 wt. % Pr and approximately 24.9 wt. % Nd, wherein the aforementioned process is carried out such will produce a permanent magnet having magnetic

performance criteria, namely  $H_{ci}$  and  $(BH)_{max}$  values, substantially equal to or somewhat in excess of an Fe-B-R magnet wherein the R component is comprising of only Nd and/or Pr.

5 The invention further comprises a method for producing sintered permanent magnets. In particular, the invention also comprises a process for preparing a sintered permanent magnetic material of the Fe-B-R type, said process comprising:

- 10 (a) preparing a metallic powder having a mean particle size of 0.3-80 microns, preferably no more than 4.0 microns, wherein the metallic powder essentially consists of a composition consisting of 15-16 atomic % R, wherein R essentially consists of the light rare earths Nd, Pr, and Ce, wherein Ce is between 0.1-5.0 wt. % of said R and preferably 0.5% of R, and preferably approximately 74% Pr and 25% Nd; 4-24 atomic % B and preferably 6.5 atomic % B; and at least 52 atomic % Fe and preferably 78 atomic %;
- 15 (b) compacting said powder at a pressure of at least 1.5 ton/cm<sup>2</sup>;
- (c) sintering the resulted body at a temperature of 900-1200 °C in a non-oxidizing or reducing atmosphere.

#### BRIEF DESCRIPTION OF THE DRAWINGS

20 The following drawings show particular embodiments of the present invention in which;

Fig 1 is a graph of selected results from Table I, showing intrinsic coercive force  $H_{ci}$  of a permanent magnet material of the Fe-B-R type as a function of Praseodymium composition of R, at Cerium concentrations of 0.5% of R;

Fig. 2 is a graph of selected results from Table I, showing intrinsic coercive force  $H_{ci}$  of a permanent magnet material of the Fe-B-R type as a function of Praseodymium composition of R, at Cerium concentrations between 5.0-5.3 % of R;

5 Fig. 3 is a graph similar to Fig. 4, showing selected result from Table I, plotting intrinsic coercive force  $H_{ci}$  of a permanent magnet material of the Fe-B-R type as a function of Cerium composition of R, at Praseodymium concentrations between 22.5 and 25% of R;

10 Fig. 4 is a graph similar to Fig. 3 showing selected result from Table I, plotting intrinsic coercive force  $H_{ci}$  of a permanent magnet material of the Fe-B-R type as a function of Cerium composition of R, at Praseodymium concentrations between 50-60% of R, and

15 Fig. 5 is a graph similar to Fig. 4, showing selected result from Table I, plotting intrinsic coercive force  $H_{ci}$  of a permanent magnet material of the Fe-B-R type as a function of Cerium composition of R, at Praseodymium concentrations between 74.6-100% of R.

#### DETAILED DESCRIPTION OF THE INVENTION

20 Because the rare earth Ce typically occurs naturally in combination with Nd and Pr and because of the cost advantages in reducing the concentration of Nd in rare earth permanent magnets, the applicant has experimented with permanent magnets of the Fe-B-R type having various concentrations of Cerium as part of the rare earth component. The applicant has further varied the relative ratios and concentration of Nd and/or Pr of the rare earth component in relation to the amount of Ce, and measured the  
25 resultant magnetic properties of the Fe-B-R permanent magnets so created.



Table I sets out the results for 35 samples of Fe-B-R type permanent magnets, where the composition of R was varied by utilizing various ratios of Ce, Pr, and Nd.

Table I

	Pr	Ce	Nd	H <sub>cl</sub>
Test Sample	(wt % of R)	(wt. % of R)	(wt. % of R)	(kOe)
B1-1	24.9	0.5	74.7	11.1
B1-2	24.9	0.5	74.7	11.3
B1-3	24.9	0.5	74.7	9.7
B2-1	24.0	4.0	72.0	9.5
B2-2	24.0	4.0	72.0	9.3
B2-3	24.0	4.0	72.0	9.8
B3-1	22.5	10.0	67.5	5.8
B3-2	22.5	10.0	67.5	6.2
B3-3	22.5	10.0	67.5	6.1
B4-1	4.5	0.5	95.0	10.0
B4-2	4.5	0.5	95.0	10.3
B4-3	4.5	0.5	95.0	10.3
B5-1	74.6	0.5	24.9	13.3
B5-2	74.6	0.5	24.9	10.5

B5-3	74.6	0.5	24.9	10.5
E0	0.0	0.0	100.0	11.1
E1	25.0	0.0	75.0	11.2
E2	24.0	4.0	72.0	10.0
E3	22.5	10.0	67.5	5.8
E4	4.5	0.5	95.0	11.5
E5	74.6	0.5	24.9	15.7
E6	48.6	5.3	46.2	9.5
E7	53.8	4.3	41.9	11.7
E-A	50.0	10.0	40.0	6.6
E-B1	60.0	0.0	40.0	11.7
E-B2	60.0	0.0	40.0	12.1
E-C1	90.0	10.0	0.0	7.7
E-C2	90.0	10.0	0.0	7.2
E-D1	100.0	0.0	0.0	9.8
E-D2	100.0	0.0	0.0	10.7
E-AB1	55.0	5.0	40.0	7.9

E-AB2	55.0	5.0	40.0	9.0
E-CD1	95.0	5.0	0.0	9.0
E-CD2	95.0	5.0	0.0	9.3
E-ABCD	75.0	5.0	20.0	7.7

5 Figs. 1-5 appended hereto are graphical plots of selected data from Table I, compiled for the purposes of assisting in interpreting the data in Table I and showing trends in magnetic performance arising from the various compositions of the R component of the 78 Fe-B 6.5-R 15.5 permanent magnet alloy compositions tested.

Individual plots of the data are made for magnetic performance  $H_{ci}$  versus Ce concentration, at constant or substantially constant values of Pr and Nd %, the percentage Nd being simply  $(100-[Ce]-[Pr])\%$ . Fig 3 shows a  
 10 plot of magnetic performance  $H_{ci}$  as a function of Cerium addition, at relatively constant values of Pr (from 22.5 to 25% wt. of R).

Fig. 4 shows a plot of magnetic performance  $H_{ci}$  as a function of Cerium addition, at relatively constant values of Pr (from 50-60 wt. %). Fig 5 likewise shows a plot of magnetic performance  $H_{ci}$  as a function of Cerium  
 15 addition, at relatively constant values of Pr (from 74.6 to 100%).

In each of the aforementioned cases, as seen from Figs. 3-5, it can broadly be said addition of Cerium, at least in the ranges between 5-10%, will cause a reduction in  $H_{ci}$ , from a value of 10-12 kOe at Ce=0% to a range of 6.1-7.8 range when Ce=10% of R.

Importantly, however, from a perusal Table I and Figs. 3-5, the applicant has observed that for ranges of Cerium addition over 0% and up to about 5%, the reduction in magnetic performance ( $H_{ci}$ ) is not that significant, and in some cases, the lower ranges of  $H_{ci}$  at Ce=0% are exceeded by some of the upper ranges of  $H_{ci}$  at Ce concentrations between 4-5%.

Analysis in the trends reflected in the data set out in Table I produce another surprising result. In particular, plots of  $H_{ci}$  as a function of Pr (wt. %) where Ce amount is kept approximately constant generally tended to show an increase in magnetic performance  $H_{ci}$  as the percentage of Pr was increased, at least for ranges of Ce concentrations at 0.5% and 10%.

Figs. 1 and 2 show a plot of the magnetic performance of the sample, as measured by  $H_{ci}$ , as a function of Pr addition, for ranges of Ce=0.5% (Fig. 1) and Ce=5.0-5.3% (Fig. 2). For Ce=5.0-5.3% (Fig. 2), as may be seen from Fig. 2, substituting Pr for Nd and generally increasing the concentration of Pr from 48% to 95% (i.e. reducing Nd from 47% to 0%) had an average, as seen from a "best fit" line plotted in Fig. 2, no effect on  $H_{ci}$ .

In the case of Ce=5% (Fig. 1) increasing Pr from 4.5% to 74.6% created an increase in  $H_{ci}$  from an average of 10.5 kOe [i.e.  $(10.0+10.3+10.3+11.5)/4$ ] to an average of 12.5 kOe [i.e.  $(13.3+10.5+10.5+15.7)/4$ ]. Because the decrease in  $H_{ci}$  caused by adding Ce was not significant at Ce=0.5%, such addition of Pr up to in substitution of Nd, wherein Pr/Nd=3:1 appears to surprisingly have caused  $H_{ci}$  to exceed the  $H_{ci}$  for permanent magnets with no Ce added. In particular, the average  $H_{ci}$  for Ce=5%, with Pr=74.6 and Nd=24.9%, was found to be 12.5 kOe, whereas, as stated earlier, average  $H_{ci}$  for ranges of Pr and Nd with no Cerium added was only found to be 11.1 kOe. Indeed, the maximum  $H_{ci}$

value of 15.7 kOe (at Pr=74.6% and Ce=0.5%) far exceeded the maximum value of  $H_{ci}$  of 12.1 kOe where Ce=0.0%.

The manner of preparing the test specimens and obtaining the data of Table I will now be described.

5           (1) The raw material for each respective magnet sample containing the predetermined respective composition was measured out and melted by high frequency induction. The obtained melt was cast in a cooled mold to obtain an ingot specimen.

10           (2) The resulting ingot specimen was crushed, and subsequently finely pulverized in a ball mill, until powders having a particle size of 0.3 to 80 microns were obtained.

          (3) A magnetic field of 7 to 20 kOe was thereafter applied to the milled powders to co-align each powder particle;

15           (4) The powders were subsequently compacted at a pressure of 1.5 Ton/cm<sup>2</sup> to produce a compacted body with a resultant density of approximately 6g/cm<sup>2</sup>;

          (5) The compacted body was sintered in an inert gas atmosphere at a temperature of 1120 °C for 2 hours.

20           (6) Values of  $H_{ci}$  were then measured for each of the individual samples, and recorded in Table I.

It is recommended that the magnetic field applied to the powders to co-align the powder particles be at least 7 kOe. Further, the magnetic field that is applied to the powder may have a range of about 7 to

about 30 kOe. In another embodiment, the magnetic field may range from about 7 to about 20 kOe.

5 The Fe-B-R magnet of the present invention containing Cerium in certain defined percentages may be prepared by the powder metallurgical sintering procedure used in preparation of the aforementioned samples. A description of the applicant's process, insofar as it relates to a process for the manufacture of the applicant's new composition, is set out below.

10 A metallic powder having a mean particle size of 0.3-80 microns, preferably less than 10 microns, is formed from a composition consisting of

- i) 13-19 atomic % R, preferably 15.16 atomic % R, wherein R essentially consists of the light rare earths Nd and/or Pr, and Ce, wherein Ce is between 0.2 to 5.0 wt. %, and preferably 0.5%, the balance of R essentially consists of Nd and Pr, and preferably approximately 74.6% Pr and 24.9% Nd.
- 15 ii) 4-8 atomic % B; preferably 6.5 atomic % B; and
- iii) the balance, preferably 78 atomic % Fe.

Such powder may be produced by known ball milling procedures, or Alpine jet milling. Since the distribution of particle size of the powder made by ball milling is wider than with powders made from Alpine jet mill, which definitely affects magnet alignment, Br, and thus  $(BH)_{max}$ , the latter set milling procedure is preferred.

20

The resultant powder may optionally be exposed to a magnetic field, of a strength equal to 7.0 to 20 kOe as in the case of the sample specimens. The metallic powder is then compacted at a pressure of at least

1.5 ton/cm<sup>2</sup> to produce a resultant compacted body having a density of at least 5g/cm<sup>2</sup>.

5 The resulting compacted body is then sintered in a reducing as or inert gas atmosphere, or as in a vacuum, at a temperature between 900-1200 °C, and preferably between 1000-1180 °C, for a period of 15 minutes to 8 hours and preferably for at least 1 hour.

10 While there have been described herein what are considered to be preferred and exemplary embodiments of the present invention, other modifications of the invention will now be apparent to those skilled in the art from the teachings herein. For a complete definition of the scope of the invention, reference is to be made to the appended claims.

Accordingly, what is desired to be secured by Letters patent is the invention as defined and differentiated in the following claims.



We claim:

1. A high performance permanent magnetic material of the Fe-B-R type, said material essentially consisting of:

5 (i) 13-19 atomic % R, where R essentially consists of a mixture of rare earth elements Nd, Pr, and Ce wherein Ce is between approximately 0.2% and no more than 5.0 wt. % of R, Pr is between about 70-76% and Nd is 29.8-23.8%;

(ii) 4-20 atomic % B;

(iii) the balance comprising Fe with impurities.

10 2. The permanent magnetic material of the Fe-B-R type as claimed in claim 1, wherein Ce is approximately 0.5-5.0 wt. % of R.

3. The permanent magnetic material of the Fe-B-R type as claimed in claim 1, wherein R 14.0-16.0 atomic %.

15 4. The permanent magnetic material of the Fe-B-R type as claimed in claim 1, wherein B is 5.0-7.0 atomic %.

5. The permanent magnetic material of the Fe-B-R type as claimed in claim 1, R essentially consisting of Pr and Nd in an approximate 3:1 ratio respectively (by weight %).

20 6. The permanent magnetic material as claimed in claim 1 when used in a magnetic resonance imaging (MRI) apparatus.

7. The permanent magnetic material of the Fe-B-R type as claimed in claim 1, wherein Pr is at least 70% of R, Ce is 0.5-3.0% wt. % of R, and the remaining percentage of R is essentially Nd.

5 8. The permanent magnetic material of the Fe-B-R type as claimed in claim 7, wherein Pr is approximately 74.6% of R, Ce is approximately 0.5% of R, and the remaining percentage of R consists essentially of Nd.

9. The permanent magnetic material of the Fe-B-R type as claimed in claim 4, wherein B is approximately 6.5 atomic %.

10 10. The permanent magnetic material of the Fe-B-R type as claimed in claim 9, wherein R is approximately 15.5 atomic %.

11. A process for preparing a sintered permanent magnetic material of the Fe-B-R type, said process comprising the steps of:

15 (a) preparing a metallic powder having a mean particle size of 0.3-80 microns said metallic powder formed from a composition consisting of 15-16 atomic % R, wherein R essentially consists of the light rare earths Nd, Pr, and Ce, wherein Ce is between 0.2-5.0 wt. % of said R, the balance of R essentially consisting of Nd and Pr where Pr is between about 70-76%, Nd is between 28.9-23.8%; 4-8 atomic % B; and at least 52 atomic % Fe;

20 (b) compacting said powder at a pressure of at least 1.5 ton/cm<sup>2</sup>;

(c) sintering the resulted body at a temperature of 900-1200 °C in a non-oxidizing or reducing atmosphere.

12. The process as claimed in claim 11, wherein said metallic powder is prepared by melting metallic material, cooling the resultant alloy, and pulverizing the alloy to form said metallic powder.

13. The process as claimed in claim 12, wherein said step of  
5 pulverizing the alloy comprises ball milling the alloy to form said powder.

14. The process as claimed in claim 12, wherein said step of pulverizing the alloy comprises jet milling the alloy to form said powder.

15. The process as claimed in claim 11, further comprising the step, while compacting said powder, applying a magnetic field of at least  
10 7 kOe.

16. The process as claimed in claim 15 wherein said metallic powder is prepared by milling to produce a mean particle size no more than 10.0 microns.

17. A sintered permanent magnetic material of the Fe-B-R type when made in accordance with the following process, namely;  
15

(a) preparing a metallic powder having a mean particle size of 0.3-80 microns, said metallic powder formed from a composition consisting of 15-16 atomic % R, wherein R essentially consists of the light rare earths Nd, Pr, and Ce, wherein Ce is between 0.2-5.0 wt. % of said R, the balance of R  
20 essentially consisting of Nd and Pr; 4-48 atomic % B, and at least 52 atomic % Fe;;

(b) compacting said powder at a pressure of at least 1.5 ton/cm<sup>2</sup>;

(c) sintering the resulted body at a temperature of 900-1200 C in a non-oxidizing or reducing atmosphere.

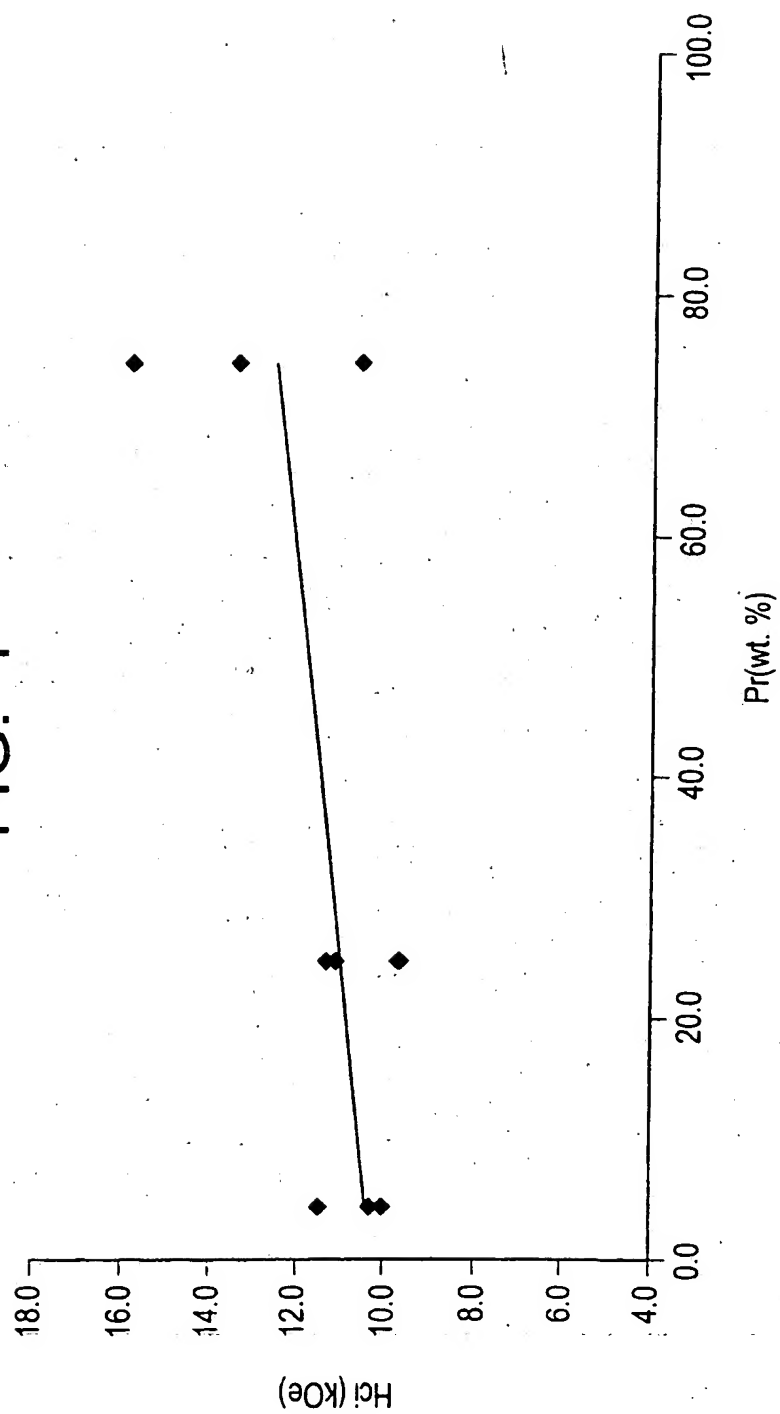
18. The permanent magnetic material as claimed in claim 17, wherein R comprises at least 70% Pr, and B comprises 5-7 atomic %.

5 19. The permanent magnetic material as claimed in claim 18, wherein the resulting body is sintered at a temperature of 1000-1180 C.

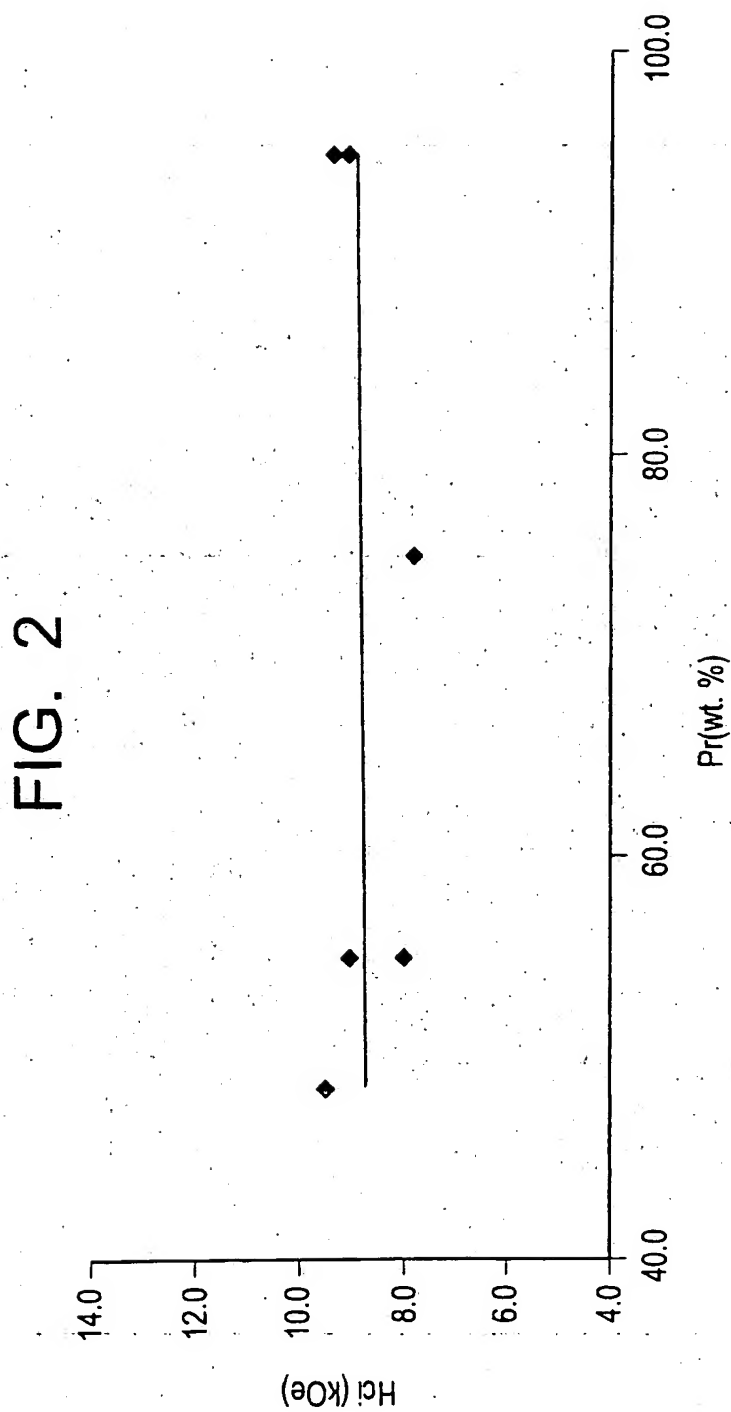
20. The permanent magnetic material as claimed in claim 18, wherein said metallic powder is prepared by milling to produce a mean particle size no more than 7.0 micron

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FIG. 1

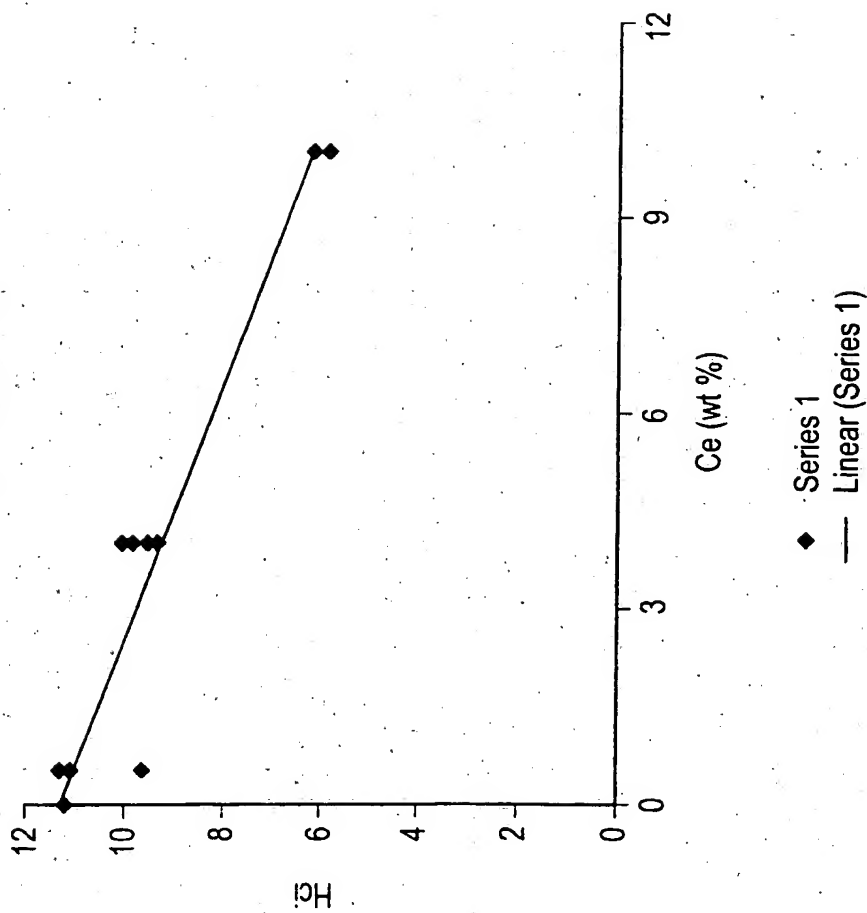


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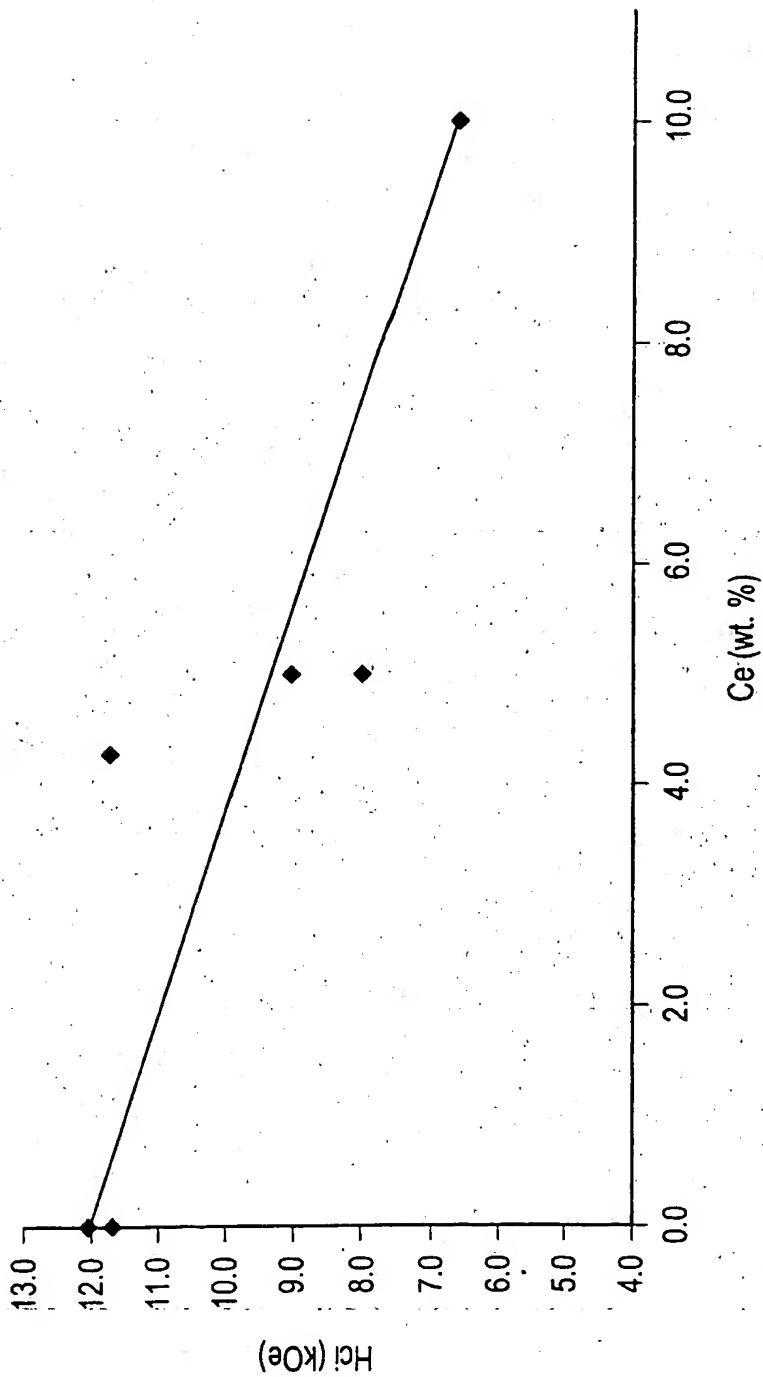
3 / 5

FIG. 3



4 / 5

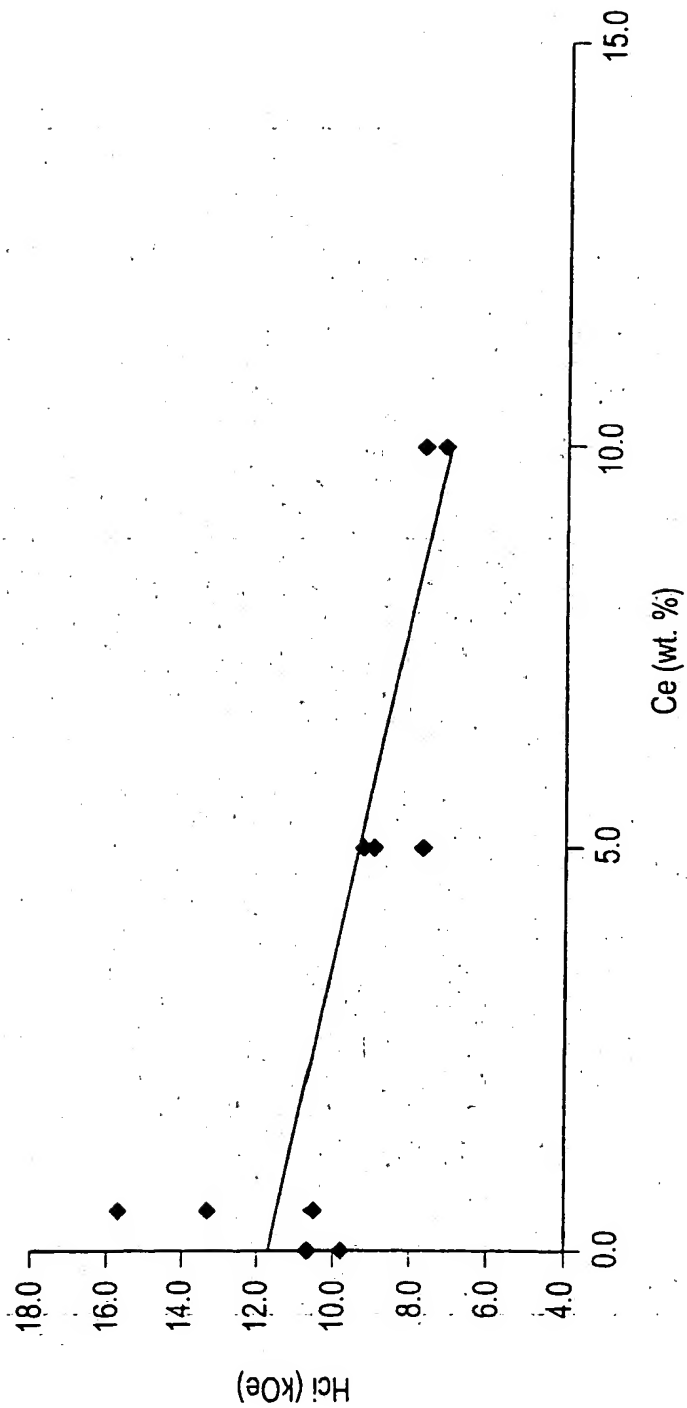
FIG. 4





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FIG. 5



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/02649

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01F1/057

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 908 076 A (IIJIMA KENZABUROU ET AL) 13 March 1990 (1990-03-13) column 3, line 16 - line 21; claim 1; example 1	1,11-13, 15-17
A	SEQUEIRA W P ET AL: "THE MAGNETIC PROPERTIES OF NANOCRYSTALLINE MELT SPUN IRON-DIDYMIUM-BORON ALLOYS" MATERIALS LETTERS, NL, NORTH HOLLAND PUBLISHING COMPANY, AMSTERDAM, vol. 15, no. 5 / 06, 1 January 1993 (1993-01-01), pages 376-378, XP000355223 ISSN: 0167-577X page 376, column 1 page 378, column 2; figure 1 -/-	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

28 April 2000

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Name and mailing address of the ISA

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/02649

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 1995, no. 03, 28 April 1995 (1995-04-28) & JP 06 346200 A (DAIDO STEEL CO LTD), 20 December 1994 (1994-12-20) abstract ----	1
A	EP 0 286 357 A (FORD WERKE AG ; FORD FRANCE (FR); FORD MOTOR CO (GB)) 12 October 1988 (1988-10-12) -----	

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. .onal Application No

PCT/US 00/02649

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			BR 8801585 A	08-11-1988
			JP 63262805 A	31-10-1988
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CORRECTED VERSION

(19) World Intellectual Property Organization  
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(10) International Publication Number  
**WO 00/48208 A1**

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99 1 02207.6 12 February 1999 (12.02.1999) CN
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- (81) Designated States (*national*): AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
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(54) Title: PERMANENT MAGNETIC MATERIALS OF THE R-FE-B TYPE AND PROCESS OF MANUFACTURE

(57) Abstract: An Fe-B-R type permanent magnetic, consisting of: 13-19 atomic % R, where R essentially consists of a mixture of rare earth elements Nd and/or Pr, and Ce, where Ce is between 0.2 and 5.0 wt. % of R; 4-20 atomic % B, and the balance comprising Fe. In a preferred aspect, R comprises 15-16 atomic % B; of which Ce is approximately 0.5 % and the remaining rare earths Pr and Nd are in a ratio of 3:1. A process of producing an Fe-B-R permanent magnet as described above, and an Fe-B-R magnetic material made by such process, are also disclosed.

PERMANENT MAGNETIC MATERIALS OF THE Fe-B-R TYPE,  
CONTAINING Ce and Nd AND/OR Pr, AND PROCESS OF  
MANUFACTURE

BACKGROUND OF THE INVENTION

5           The present invention relates to magnetic material compositions and a process for their manufacture, and more particularly performance magnetic material of the iron-boron-rare earth type (Fe-B-R).

          Use of high performance permanent magnets of Fe-B-R type, where R is a rare earth element containing high concentrations of the element  
10   Neodymium (Nd) has become common in industry since the early 1980's. For example, computer hardware manufacturers who manufacture small footprint, large capacity computer data storage and retrieval hardware need permanent magnets in such devices. Due to severe size and weight restrictions inherent in such data storage devices, the permanent magnets  
15   contained therein must be relatively small yet have very strong magnetic properties to generate the required magnetic field. This has necessitated the use of very high performance Fe-B-R rare-earth permanent magnets within such devices.

          In addition, medical diagnostic devices in the medical field,  
20   namely, magnetic resonance imaging (MRI) devices employ vast quantities (up to 1.5 tons) of permanent magnetic material, typically Fe-B-R magnets which contain high percentages of the rare earth Nd as the rare earth component.

          Accordingly, due to the sale of these devices since the early  
25   1980's employing Fe-B-R permanent magnets wherein the rare earth

component is principally comprised of Nd, the worldwide demand for Nd has increased. As a result, the cost of the raw material Nd used in manufacture of such permanent magnets has greatly increased.

5 A real need has arisen to develop Fe-B-R magnets of substantially equal performance, which utilize less Nd to thereby reduce the cost of the manufacture of such magnets and the devices which contain such magnets.

Permanent magnets of the Fe-B-R type, where R is one or more rare earth elements of which at least 50% of R is Nd and/or Praseodymium (Pr), are known. For example, U.S. Patents 4,684,406 and 4,597,938 both teach  
10 a high performance sintered permanent magnetic material of the Fe-B-R type. Such patents teach a high performance magnet consisting of, by atomic percent, (i) 12.5%-20% R wherein R is at least one rare earth element (selected from the group consisting of Nd, Pr, La, Ce, Tb, Dy, Ho, Er, Eu, Sm, Gd, Pm,  
15 Tm, Yb, Lu and Y) and at least 50% of R consists of Nd and/or Pr; (ii) 4-20%B; and (iii) the balance Fe with impurities. Likewise, as may be seen from U.S. 4,597,938, U.S. 4,975,130 and U.S. 4,684,606, such patents teach a process of preparing such a permanent magnet comprising forming powders of alloys of the above composition; melting same to form an ingot; pulverizing the ingot  
20 to form an alloy powder having a mean particle size from 0.3 to 80 microns; compacting such powder at a pressure of 0.5 to 8 Ton/cm<sup>2</sup>; subjecting the compacted body to a magnetic field of about 7 to 13 kOe; and lastly sintering at a temperature between 900 to 1,200 °C (preferably 1,000 to 1,180 °C). A permanent magnet prepared in the above fashion specifically comprised of 77  
25 Fe-9 B-9 Nd-5 Pr (wherein Nd and Pr together comprise the rare earth component), sintered at 1,120 °C for four hours in an inert atmosphere can

acquire a high maximum energy product  $(BH)_{\max}$  of approximately 31.0 MGOe. Likewise, a permanent magnet comprised of 79 Fe-7 B-14 Nd, sintered at 1,120 °C for one hour at (atmosphere), can acquire a maximum energy product  $(BH)_{\max}$  of approximately 33.8 MGOe (ref. Table 1, U.S. 4,975,130). A sintered permanent magnet comprising 77Fe-7B-16Pr, sintered at 1,040 °C in a vacuum at  $1 \times 10^{-4}$  torr for two hours can be produced having a maximum energy product somewhat less, namely, 24.5 MGOe.

None of these prior art patents disclose or suggest what significance, if any, the amount of Ce present or the concentration of Ce as part of R may have on Fe-B-R magnet performance. Nor does the prior art teach or suggest ranges of concentrations of Ce which may form part of the rare earth component of an Fe-B-R magnet in substitution for Nd which will give equal or better magnetic performance of an Fe-B-(Nd and/or Pr) permanent magnet.

## SUMMARY OF THE INVENTION

Applicants have discovered that relatively small percentages of Cerium, which in any event usually naturally occur in rare earth deposits containing Nd, may be included in certain defined percentages as part of the rare earth component "R" of an Fe-B-R magnet. R additionally comprises 70-76% Pr, 29.8-23.8% Nd and up to and including 5% Ce with no significant or only slight decrease in the magnetic performance of the resultant permanent magnet.

The applicants have further discovered that when certain low percentages of Cerium (0.5% wt. of R) are used in manufacture of an Fe-B-R permanent magnet in substitution of Nd, further substitution of Nd may



further be made with Pr up to 76% which further substitution, particularly at Pr = 75%, will not reduce, and indeed appears to substantially equal or even enhance, the magnetic performance characteristics over a magnetic material made up of the same total percentage of rare earth elements but lacking Ce, or having Ce but having higher concentrations of Nd.

By substitution of portions of Nd with specific small percentages of Ce and greater amounts of Ce in accordance with the invention herein disclosed, significant cost savings can be achieved in the manufacture of high performance permanent magnets of the Fe-B-R type, while substantially maintaining the magnetic performance of the magnet. Even in respect of certain concentrations of added or entrained Ce which may cause a reduction in the magnetic performance of the Fe-B-R magnetic material as compared with Fe-B-R magnetic material which employs substantially pure Nd, additional magnetic material having Ce and Pr as described herein can be used so as to make up the deficit in strength of magnetic field required in an MRI device.

Accordingly, in one broad aspect the applicants' invention comprises a high performance permanent magnetic material of the Fe-B-R type, said material essentially consisting of:

(i) 13-19 atomic % R, where R comprises a mixture of rare earth elements Nd, Pr, and Ce wherein Ce is between approximately 0.2% and no more than 5.0 wt. % of R and Pr is between 70-76% and 29.8-23.8% Nd;

(ii) 4-20 atomic % B;

(iii) the balance comprising Fe with impurities.

In preferred embodiments, the Fe-B-R magnet of the present invention essentially consisted of, by atomic %, 15-16 % R, with Ce comprising 0.5-3 wt. %, and preferably 0.5%, with the remainder of R essentially consisting of Pr and/or Nd, preferably in the order of about 71.6% Pr and 24.9 % Nd, i.e. a 3:1 ratio.

The present invention further comprises a sintered permanent magnetic material of the Fe-B-R type when made in accordance with the following process, namely:

- (a) preparing a metallic powder having a mean particle size of 0.3-80 microns, said metallic powder formed from a composition essentially consisting of 15-16 atomic % R, wherein R essentially consists of the light rare earths Nd, Pr, and Ce, wherein Ce is between 0.2-5.0 wt. % of said R, the balance of R essentially consisting of 29.8-23.8% Nd and 70-76% Pr; 4-8 atomic % B, and at least 52 atomic % Fe;
- (b) compacting said powder at a pressure of at least 1.5 ton/cm<sup>2</sup>;
- (c) sintering the resulted body at a temperature of 900-1200 °C in a non-oxidizing or reducing atmosphere.

In addition, the applicants have found that while adding Cerium generally tends to decrease magnetic performance of Fe-B-R magnets having only Nd, by substituting Pr for Nd where Ce concentration is low will cause a substantial restoration of lost magnetic performance. Accordingly, the applicant has found that using low concentrations of Ce (0.5% wt.) of R with the balance of R essentially consisting of approximately 74.6 wt. % Pr and approximately 24.9 wt. % Nd, wherein the aforementioned process is carried out such will produce a permanent magnet having magnetic

performance criteria, namely  $H_{ci}$  and  $(BH)_{max}$  values, substantially equal to or somewhat in excess of an Fe-B-R magnet wherein the R component is comprising of only Nd and/or Pr.

5 The invention further comprises a method for producing sintered permanent magnets. In particular, the invention also comprises a process for preparing a sintered permanent magnetic material of the Fe-B-R type, said process comprising:

- 10 (a) preparing a metallic powder having a mean particle size of 0.3-80 microns, preferably no more than 4.0 microns, wherein the metallic powder essentially consists of a composition consisting of 15-16 atomic % R, wherein R essentially consists of the light rare earths Nd, Pr, and Ce, wherein Ce is between 0.1-5.0 wt. % of said R and preferably 0.5% of R, and preferably approximately 74% Pr and 25% Nd; 4-24 atomic % B and preferably 6.5 atomic % B; and at least 52 atomic % Fe and preferably 78 atomic %;
- 15 (b) compacting said powder at a pressure of at least 1.5 ton/cm<sup>2</sup>;
- (c) sintering the resulted body at a temperature of 900-1200 °C in a non-oxidizing or reducing atmosphere.

#### BRIEF DESCRIPTION OF THE DRAWINGS

20 The following drawings show particular embodiments of the present invention in which;

Fig 1 is a graph of selected results from Table I, showing intrinsic coercive force  $H_{ci}$  of a permanent magnet material of the Fe-B-R type as a function of Praseodymium composition of R, at Cerium concentrations of 0.5% of R;

Fig. 2 is a graph of selected results from Table I, showing intrinsic coercive force  $H_{ci}$  of a permanent magnet material of the Fe-B-R type as a function of Praseodymium composition of R, at Cerium concentrations between 5.0-5.3 % of R;

5 Fig. 3 is a graph similar to Fig. 4, showing selected result from Table I, plotting intrinsic coercive force  $H_{ci}$  of a permanent magnet material of the Fe-B-R type as a function of Cerium composition of R, at Praseodymium concentrations between 22.5 and 25% of R;

10 Fig. 4 is a graph similar to Fig. 3 showing selected result from Table I, plotting intrinsic coercive force  $H_{ci}$  of a permanent magnet material of the Fe-B-R type as a function of Cerium composition of R, at Praseodymium concentrations between 50-60% of R, and

15 Fig. 5 is a graph similar to Fig. 4, showing selected result from Table I, plotting intrinsic coercive force  $H_{ci}$  of a permanent magnet material of the Fe-B-R type as a function of Cerium composition of R, at Praseodymium concentrations between 74.6-100% of R.

#### DETAILED DESCRIPTION OF THE INVENTION

20 Because the rare earth Ce typically occurs naturally in combination with Nd and Pr and because of the cost advantages in reducing the concentration of Nd in rare earth permanent magnets, the applicant has experimented with permanent magnets of the Fe-B-R type having various concentrations of Cerium as part of the rare earth component. The applicant has further varied the relative ratios and concentration of Nd and/or Pr of the rare earth component in relation to the amount of Ce, and measured the  
25 resultant magnetic properties of the Fe-B-R permanent magnets so created.

Table I sets out the results for 35 samples of Fe-B-R type permanent magnets, where the composition of R was varied by utilizing various ratios of Ce, Pr, and Nd.

Table I

	Pr	Ce	Nd	H <sub>Cl</sub>
Test Sample	(wt % of R)	(wt. % of R)	(wt. % of R)	(kOe)
B1-1	24.9	0.5	74.7	11.1
B1-2	24.9	0.5	74.7	11.3
B1-3	24.9	0.5	74.7	9.7
B2-1	24.0	4.0	72.0	9.5
B2-2	24.0	4.0	72.0	9.3
B2-3	24.0	4.0	72.0	9.8
B3-1	22.5	10.0	67.5	5.8
B3-2	22.5	10.0	67.5	6.2
B3-3	22.5	10.0	67.5	6.1
B4-1	4.5	0.5	95.0	10.0
B4-2	4.5	0.5	95.0	10.3
B4-3	4.5	0.5	95.0	10.3
B5-1	74.6	0.5	24.9	13.3
B5-2	74.6	0.5	24.9	10.5

B5-3	74.6	0.5	24.9	10.5
E0	0.0	0.0	100.0	11.1
E1	25.0	0.0	75.0	11.2
E2	24.0	4.0	72.0	10.0
E3	22.5	10.0	67.5	5.8
E4	4.5	0.5	95.0	11.5
E5	74.6	0.5	24.9	15.7
E6	48.6	5.3	46.2	9.5
E7	53.8	4.3	41.9	11.7
E-A	50.0	10.0	40.0	6.6
E-B1	60.0	0.0	40.0	11.7
E-B2	60.0	0.0	40.0	12.1
E-C1	90.0	10.0	0.0	7.7
E-C2	90.0	10.0	0.0	7.2
E-D1	100.0	0.0	0.0	9.8
E-D2	100.0	0.0	0.0	10.7
E-AB1	55.0	5.0	40.0	7.9

E-AB2	55.0	5.0	40.0	9.0
E-CD1	95.0	5.0	0.0	9.0
E-CD2	95.0	5.0	0.0	9.3
E-ABCD	75.0	5.0	20.0	7.7

Figs. 1-5 appended hereto are graphical plots of selected data from Table I, compiled for the purposes of assisting in interpreting the data in Table I and showing trends in magnetic performance arising from the various compositions of the R component of the 78 Fe-B 6.5-R 15.5 permanent magnet alloy compositions tested.

Individual plots of the data are made for magnetic performance  $H_{ci}$  versus Ce concentration, at constant or substantially constant values of Pr and Nd %, the percentage Nd being simply  $(100 - [\text{Ce}] - [\text{Pr}])\%$ . Fig 3 shows a plot of magnetic performance  $H_{ci}$  as a function of Cerium addition, at relatively constant values of Pr (from 22.5 to 25% wt. of R).

Fig. 4 shows a plot of magnetic performance  $H_{ci}$  as a function of Cerium addition, at relatively constant values of Pr (from 50-60 wt. %). Fig 5 likewise shows a plot of magnetic performance  $H_{ci}$  as a function of Cerium addition, at relatively constant values of Pr (from 74.6 to 100%).

In each of the aforementioned cases, as seen from Figs. 3-5, it can broadly be said addition of Cerium, at least in the ranges between 5-10%, will cause a reduction in  $H_{ci}$  from a value of 10-12 kOe at Ce=0% to a range of 6.1-7.8 range when Ce=10% of R.



Importantly, however, from a perusal Table I and Figs. 3-5, the applicant has observed that for ranges of Cerium addition over 0% and up to about 5%, the reduction in magnetic performance ( $H_{ci}$ ) is not that significant, and in some cases, the lower ranges of  $H_{ci}$  at Ce=0% are exceeded by some of the upper ranges of  $H_{ci}$  at Ce concentrations between 4-5%.

Analysis in the trends reflected in the data set out in Table I produce another surprising result. In particular, plots of  $H_{ci}$  as a function of Pr (wt. %) where Ce amount is kept approximately constant generally tended to show an increase in magnetic performance  $H_{ci}$  as the percentage of Pr was increased, at least for ranges of Ce concentrations at 0.5% and 10%.

Figs. 1 and 2 show a plot of the magnetic performance of the sample, as measured by  $H_{ci}$ , as a function of Pr addition, for ranges of Ce=0.5% (Fig. 1) and Ce=5.0-5.3% (Fig. 2). For Ce=5.0-5.3% (Fig. 2), as may be seen from Fig. 2, substituting Pr for Nd and generally increasing the concentration of Pr from 48% to 95% (i.e. reducing Nd from 47% to 0%) had an average, as seen from a "best fit" line plotted in Fig. 2, no effect on  $H_{ci}$ .

In the case of Ce=5% (Fig. 1) increasing Pr from 4.5% to 74.6% created an increase in  $H_{ci}$  from an average of 10.5 kOe [i.e.  $(10.0+10.3+10.3+11.5)/4$ ] to an average of 12.5 kOe [i.e.  $(13.3+10.5+10.5+15.7)/4$ ]. Because the decrease in  $H_{ci}$  caused by adding Ce was not significant at Ce=0.5%, such addition of Pr up to in substitution of Nd, wherein Pr/Nd=3:1 appears to surprisingly have caused  $H_{ci}$  to exceed the  $H_{ci}$  for permanent magnets with no Ce added. In particular, the average  $H_{ci}$  for Ce=5%, with Pr=74.6 and Nd=24.9%, was found to be 12.5 kOe, whereas, as stated earlier, average  $H_{ci}$  for ranges of Pr and Nd with no Cerium added was only found to be 11.1 kOe. Indeed, the maximum  $H_{ci}$

value of 15.7 kOe (at Pr=74.6% and Ce=0.5%) far exceeded the maximum value of  $H_{ci}$  of 12.1 kOe where Ce=0.0%.

The manner of preparing the test specimens and obtaining the data of Table I will now be described.

5                   (1) The raw material for each respective magnet sample containing the predetermined respective composition was measured out and melted by high frequency induction. The obtained melt was cast in a cooled mold to obtain an ingot specimen.

10                   (2) The resulting ingot specimen was crushed, and subsequently finely pulverized in a ball mill, until powders having a particle size of 0.3 to 80 microns were obtained.

                  (3) A magnetic field of 7 to 20 kOe was thereafter applied to the milled powders to co-align each powder particle;

15                   (4) The powders were subsequently compacted at a pressure of 1.5 Ton/cm<sup>2</sup> to produce a compacted body with a resultant density of approximately 6g/cm<sup>2</sup>;

                  (5) The compacted body was sintered in an inert gas atmosphere at a temperature of 1120 °C for 2 hours.

20                   (6) Values of  $H_{ci}$  were then measured for each of the individual samples, and recorded in Table I.

It is recommended that the magnetic field applied to the powders to co-align the powder particles be at least 7 kOe. Further, the magnetic field that is applied to the powder may have a range of about 7 to

about 30 kOe. In another embodiment, the magnetic field may range from about 7 to about 20 kOe.

5 The Fe-B-R magnet of the present invention containing Cerium in certain defined percentages may be prepared by the powder metallurgical sintering procedure used in preparation of the aforementioned samples. A description of the applicant's process, insofar as it relates to a process for the manufacture of the applicant's new composition, is set out below.

10 A metallic powder having a mean particle size of 0.3-80 microns, preferably less than 10 microns, is formed from a composition consisting of

- i) 13-19 atomic % R, preferably 15.16 atomic % R, wherein R essentially consists of the light rare earths Nd and/or Pr, and Ce, wherein Ce is between 0.2 to 5.0 wt. %, and preferably 0.5%, the balance of R essentially consists of Nd and Pr, and preferably approximately 74.6% Pr and 24.9% Nd;
- 15 ii) 4-8 atomic % B; preferably 6.5 atomic % B; and
- iii) the balance, preferably 78 atomic % Fe.

20 Such powder may be produced by known ball milling procedures, or Alpine jet milling. Since the distribution of particle size of the powder made by ball milling is wider than with powders made from Alpine jet mill, which definitely affects magnet alignment, Br, and thus  $(BH)_{\max}$ , the latter set milling procedure is preferred.

The resultant powder may optionally be exposed to a magnetic field, of a strength equal to 7.0 to 20 kOe as in the case of the sample specimens. The metallic powder is then compacted at a pressure of at least

1.5 ton/cm<sup>2</sup> to produce a resultant compacted body having a density of at least 5g/cm<sup>2</sup>.

5 The resulting compacted body is then sintered in a reducing as or inert gas atmosphere, or as in a vacuum, at a temperature between 900-1200 °C, and preferably between 1000-1180 °C, for a period of 15 minutes to 8 hours and preferably for at least 1 hour.

10 While there have been described herein what are considered to be preferred and exemplary embodiments of the present invention, other modifications of the invention will now be apparent to those skilled in the art from the teachings herein. For a complete definition of the scope of the invention, reference is to be made to the appended claims.

Accordingly, what is desired to be secured by Letters patent is the invention as defined and differentiated in the following claims.

We claim:

1. A high performance permanent magnetic material of the Fe-B-R type, said material essentially consisting of:

5 (i) 13-19 atomic % R, where R essentially consists of a mixture of rare eaerth elements Nd, Pr, and Ce wherein Ce is between approximately 0.2% and no more than 5.0 wt. % of R, Pr is between about 70-76% and Nd is 29.8-23.8%;

(ii) 4-20 atomic % B;

(iii) the balance comprising Fe with impurities.

10 2. The permanent magnetic material of the Fe-B-R type as claimed in claim 1, wherein Ce is approximately 0.5-5.0 wt. % of R.

3. The permanent magnetic material of the Fe-B-R type as claimed in claim 1, wherein R 14.0-16.0 atomic %.

15 4. The permanent magnetic material of the Fe-B-R type as claimed in claim 1, wherein B is 5.0-7.0 atomic %.

5. The permanent magnetic material of the Fe-B-R type as claimed in claim 1, R essentially consisting of Pr and Nd in an approximate 3:1 ratio respectively (by weight %).

20 6. The permanent magnetic material as claimed in claim 1 when used in a magnetic resonance imaging (MRI) apparatus.

7. The permanent magnetic material of the Fe-B-R type as claimed in claim 1, wherein Pr is at least 70% of R, Ce is 0.5-3.0% wt. % of R, and the remaining percentage of R is essentially Nd.

5 8. The permanent magnetic material of the Fe-B-R type as claimed in claim 7, wherein Pr is approximately 74.6% of R, Ce is approximately 0.5% of R, and the remaining percentage of R consists essentially of Nd.

9. The permanent magnetic material of the Fe-B-R type as claimed in claim 4, wherein B is approximately 6.5 atomic %.

10 10. The permanent magnetic material of the Fe-B-R type as claimed in claim 9, wherein R is approximately 15.5 atomic %.

11. A process for preparing a sintered permanent magnetic material of the Fe-B-R type, said process comprising the steps of:

15 (a) preparing a metallic powder having a mean particle size of 0.3-80 microns said metallic powder formed from a composition consisting of 15-16 atomic % R, wherein R essentially consists of the light rare earths Nd, Pr, and Ce, wherein Ce is between 0.2-5.0 wt. % of said R, the balance of R essentially consisting of Nd and Pr where Pr is between about 70-76%, Nd is between 28.9-23.8%; 4-8 atomic % B; and at least 52 atomic % Fe;

20 (b) compacting said powder at a pressure of at least 1.5 ton/cm<sup>2</sup>;

(c) sintering the resulted body at a temperature of 900-1200 °C in a non-oxidizing or reducing atmosphere.

12. The process as claimed in claim 11, wherein said metallic powder is prepared by melting metallic material, cooling the resultant alloy, and pulverizing the alloy to form said metallic powder.

5 13. The process as claimed in claim 12, wherein said step of pulverizing the alloy comprises ball milling the alloy to form said powder.

14. The process as claimed in claim 12, wherein said step of pulverizing the alloy comprises jet milling the alloy to form said powder.

10 15. The process as claimed in claim 11, further comprising the step, while compacting said powder, applying a magnetic field of at least 7 kOe.

16. The process as claimed in claim 15 wherein said metallic powder is prepared by milling to produce a mean particle size no more than 10.0 microns.

15 17. A sintered permanent magnetic material of the Fe-B-R type when made in accordance with the following process, namely;

20 (a) preparing a metallic powder having a mean particle size of 0.3-80 microns, said metallic powder formed from a composition consisting of 15-16 atomic % R, wherein R essentially consists of the light rare earths Nd, Pr, and Ce, wherein Ce is between 0.2-5.0 wt. % of said R, the balance of R essentially consisting of Nd and Pr; 4-48 atomic % B, and at least 52 atomic % Fe;;

(b) compacting said powder at a pressure of at least 1.5 ton/cm<sup>2</sup>;

(c) sintering the resulted body at a temperature of 900-1200 °C in a non-oxidizing or reducing atmosphere.

18. The permanent magnetic material as claimed in claim 17, wherein R comprises at least 70% Pr, and B comprises 5-7 atomic %.

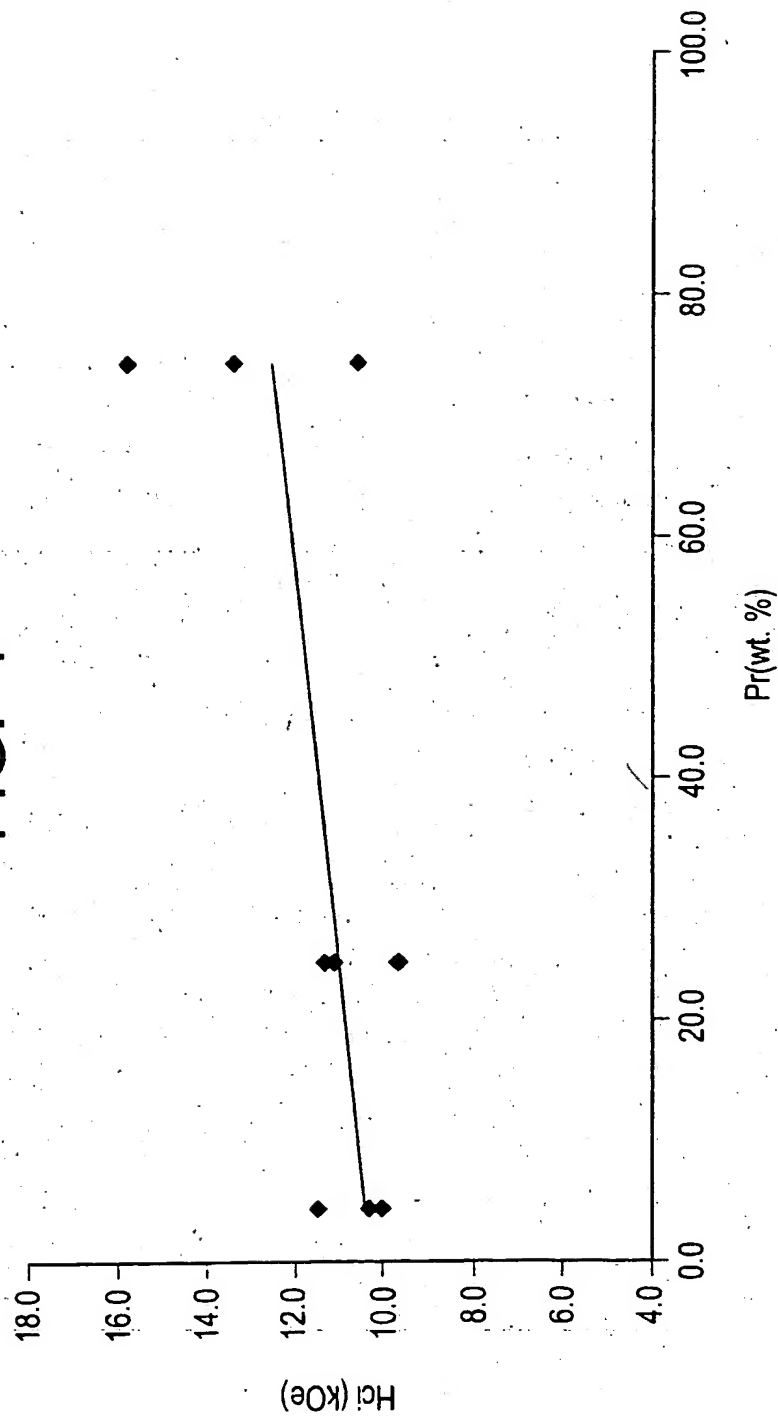
5 19. The permanent magnetic material as claimed in claim 18, wherein the resulting body is sintered at a temperature of 1000-1180 °C.

20. The permanent magnetic material as claimed in claim 18, wherein said metallic powder is prepared by milling to produce a mean particle size no more than 7.0 micron



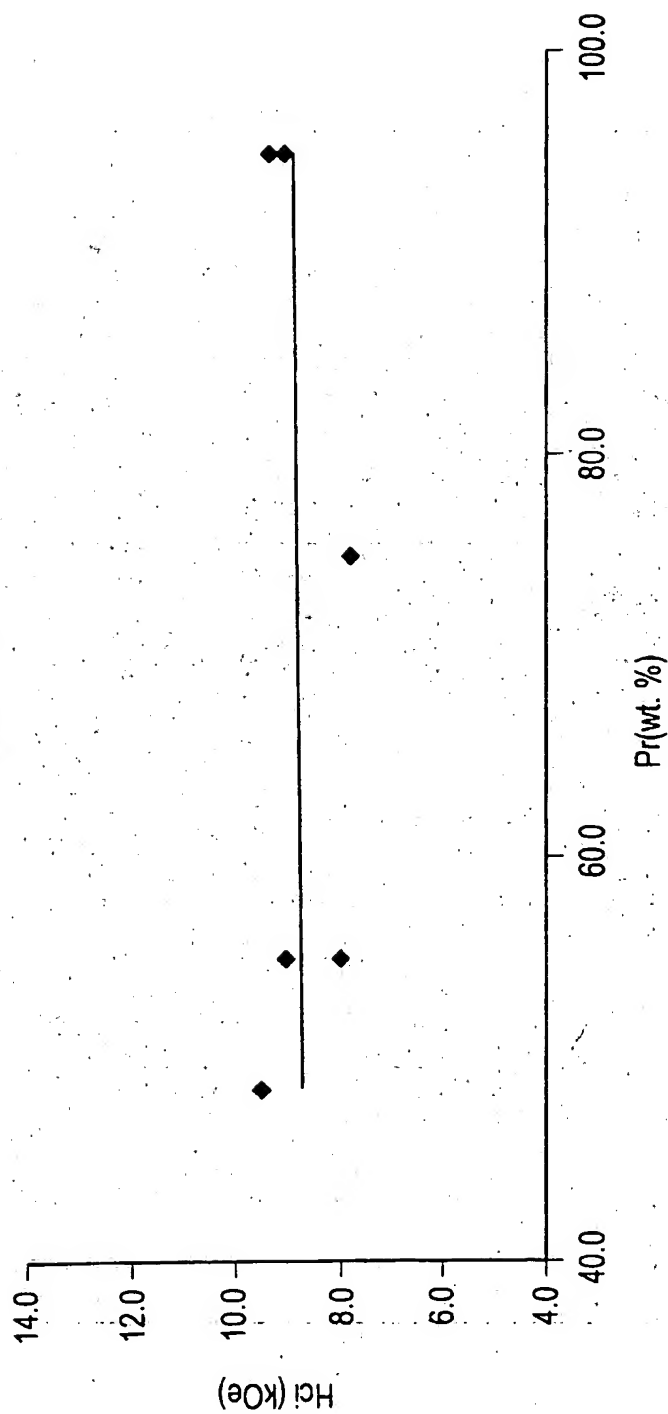
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FIG. 1



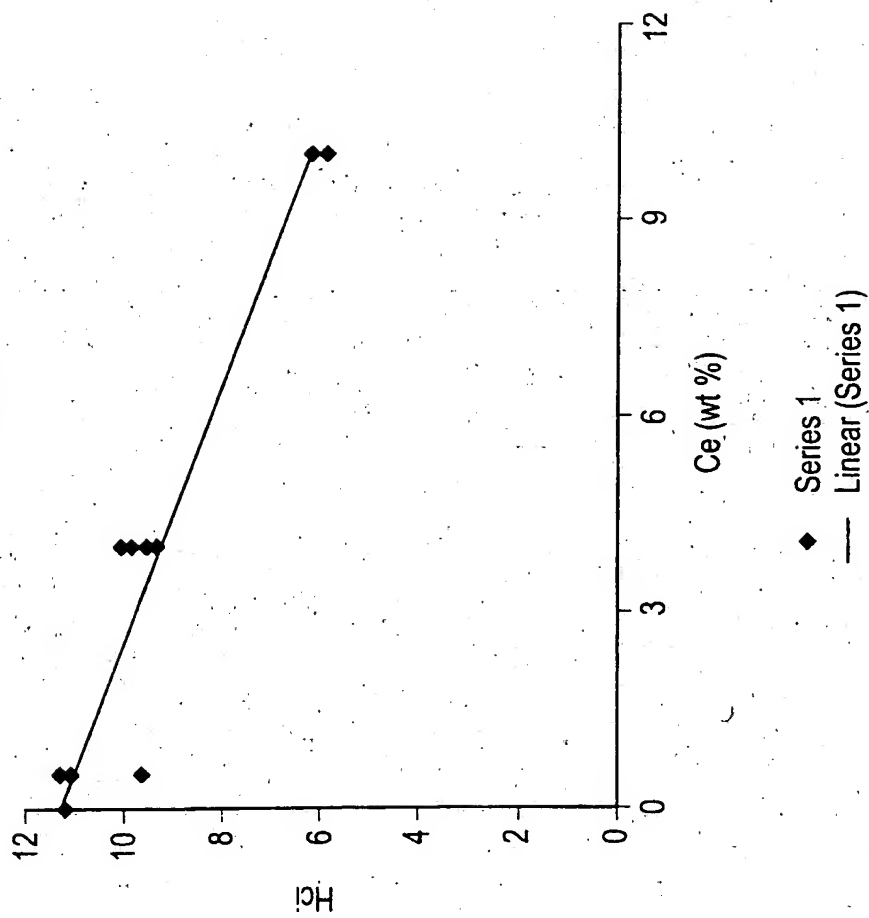
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FIG. 2



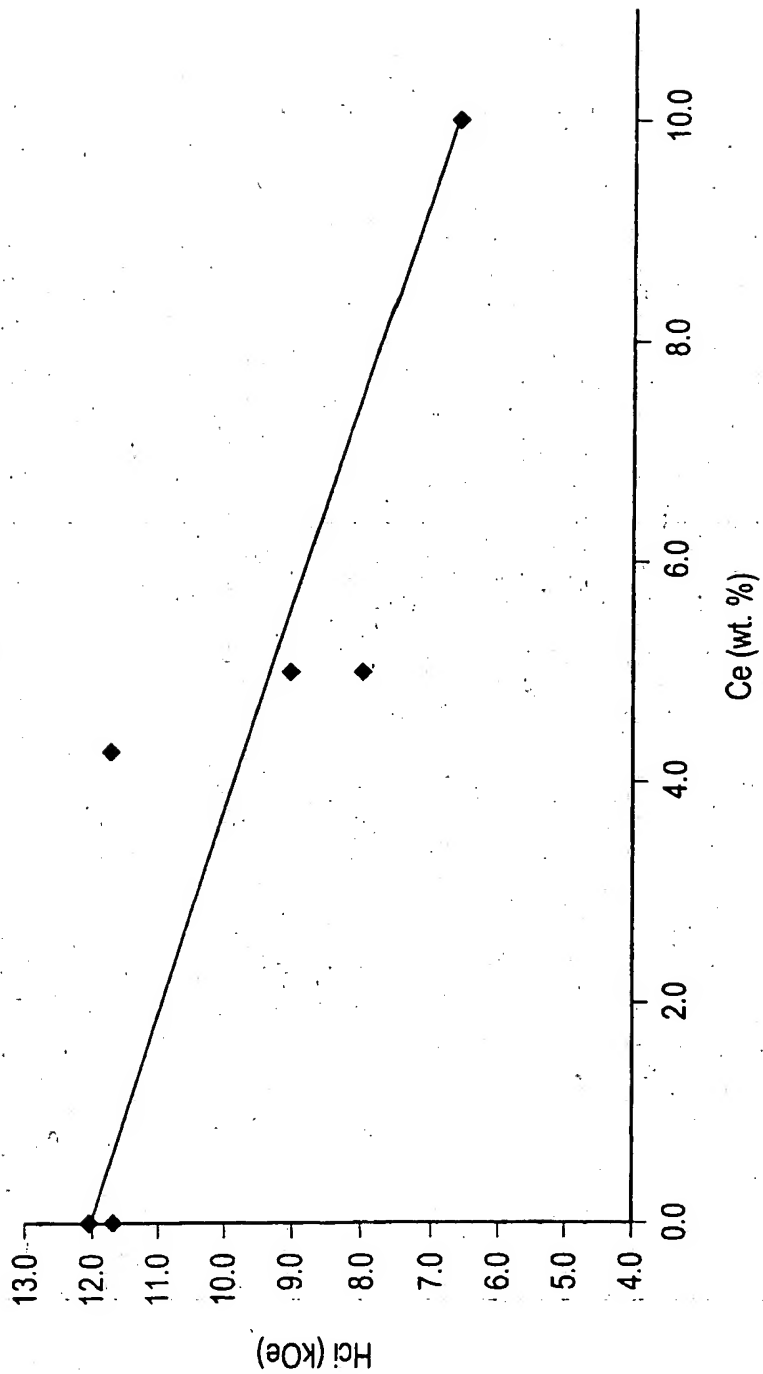
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FIG. 3



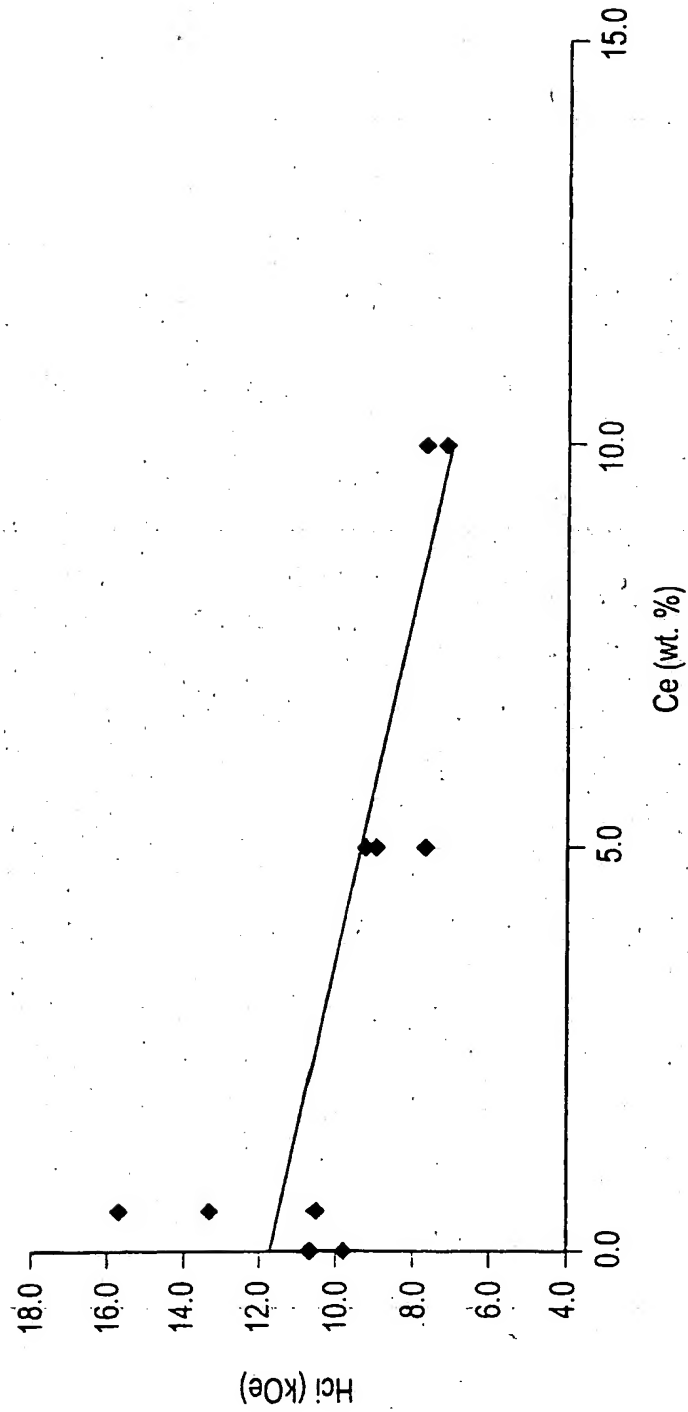
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FIG. 4



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FIG. 5



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/02649

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 H01F1/057

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 908 076 A (IIJIMA KENZABUROU ET AL) 13 March 1990 (1990-03-13) column 3, line 16 - line 21; claim 1; example 1	1, 11-13, 15-17
A	SEQUEIRA W P ET AL: "THE MAGNETIC PROPERTIES OF NANOCRYSTALLINE MELT SPUN IRON-DIDYMIUM-BORON ALLOYS" MATERIALS LETTERS, NL, NORTH HOLLAND PUBLISHING COMPANY, AMSTERDAM, vol. 15, no. 5 / 06, 1 January 1993 (1993-01-01), pages 376-378, XP000355223 ISSN: 0167-577X page 376, column 1 page 378, column 2; figure 1	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

28 April 2000

Date of mailing of the international search report

08/05/2000

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# INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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